

## Sorption behavior of U(VI) on phyllite: experiments and modeling

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Received 1 October 1999; received in revised form 25 February 2000; accepted 31 March 2000

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### Abstract

The sorption of U(VI) onto low-grade metamorphic rock phyllite was modeled with the diffuse double layer model (DDLm) using the primary mineralogical constituents of phyllite, i.e. quartz, chlorite, muscovite, and albite, as input components, and as additional component, the poorly ordered Fe oxide hydroxide mineral, ferrihydrite. Ferrihydrite forms during the batch sorption experiment as a weathering product of chlorite. In this process, Fe(II), leached from the chlorite, oxidizes to Fe(III), hydrolyses and precipitates as ferrihydrite. The formation of ferrihydrite during the batch sorption experiment was identified by Mössbauer spectroscopy, showing a 2.8% increase of Fe(III) in the phyllite powder. The ferrihydrite was present as Fe nanoparticles or agglomerates with diameters ranging from 6 to 25 nm, with indications for even smaller particles. These Fe colloids were detected in centrifugation experiments of a ground phyllite suspension using various centrifugal forces.

The basis for the successful interpretation of the experimental sorption data of uranyl(VI) on phyllite were: (1) the determination of surface complex formation constants of uranyl with quartz, chlorite, muscovite, albite, and ferrihydrite in individual batch sorption experiments, (2) the determination of surface acidity constants of quartz, chlorite, muscovite, and albite obtained from separate acid–base titration, (3) the determination of surface site densities of quartz, chlorite, muscovite, and albite evaluated independently of each other with adsorption isotherms, and (4) the quantification of the secondary phase ferrihydrite, which formed during the batch sorption experiments with phyllite. The surface complex formation constants and the protolysis constants were optimized by using the experimentally obtained data sets and the computer code FITEQL. Surface site densities were evaluated from adsorption isotherms at pH 6.5.

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The uranyl(VI) sorption onto phyllite was accurately modeled with these newly determined constants and parameters of the main mineralogical constituents of phyllite and the secondary mineralization phase ferrihydrite. The modeling indicated that uranyl sorption to ferrihydrite clearly dominates uranyl sorption, showing the great importance of secondary iron phases for sorption studies. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Surface complexation modeling; Quartz; Chlorite; Muscovite; Albite; Ferrihydrite

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## 1. Introduction

Many studies of uranyl(VI) sorption onto rock and mineral surfaces have been carried out (e.g. Ames et al., 1983; Kohler et al., 1996; Pabalan et al., 1998; Read et al., 1993). The chemical transport of contaminants through rocks, sediments, and soil is strongly influenced by sorption onto the surrounding rocks and mineral phases. The sorption term is usually described in chemical transport codes with the empirical  $K_d$ -method, in which a distribution equilibrium between solid and aqueous phase is used. This approach, however, ignores the actual species present in solution and at the mineral–water interface. Recently, the interactions of dissolved ionic species with the mineral–water interface have been interpreted and quantified by the more specific surface complexation models (SCMs) (Westall and Hohl, 1980; Davis and Kent, 1990; Dzombak and Morel, 1990; Hayes et al., 1991). SCMs define the formation of surface species via chemical reactions between surface functional groups and aqueous species (Davis and Kent, 1990), and also account for the influence of the electrostatic potential due to surface charge. These models, however, still lack a sufficient thermodynamic database of surface complex formation constants, which makes the transferability of this approach to nature very difficult. This study aims to generate such surface complex formation constants of uranyl sorbing onto quartz, chlorite, muscovite, albite, and ferrihydrite, and thereby intends to enlarge existing thermodynamic databases. The use of such databases should contribute to an improved geochemical modeling of chemical transport of toxic heavy metals.

This study was conducted in the context of the former uranium mining activities in Saxony and Thuringia, Eastern Germany, which resulted in a potential risk for public health arising from migrating uranium from underground mines, mine tailings, and tailing ponds to the nearby densely populated environment. The uranyl sorption behavior of phyllite, a common low-grade metamorphic rock from the Western Erzgebirge in Saxony, Germany and a major rock component of uranium tailings, is studied in detail. So far, the application of surface complexation theory to natural systems, i.e. composite materials, e.g. heterogeneous rocks and soil, has not yet been fully developed (Davis and Kent, 1990). However, we hypothesize that the sorption behavior of uranium onto rocks can be described in an additive fashion to the sorption onto its mineralogical components, and possibly forming secondary minerals. Secondary minerals may form from the mineral dissolution of one or more of the primary mineralogical rock components. Since the number of common rock-forming minerals is rather small, this approach should lead to fast and accurate predictions of toxic heavy metal sorption onto rocks if appropriate mineral databases are available. To verify this hypothesis, we carried out a large number

of batch sorption experiments with U(VI), acid–base titration, and adsorption isotherms with phyllite, quartz, chlorite, muscovite, albite, and ferrihydrite. Furthermore, we probed for the possible formation of secondary Fe phases by Mössbauer spectroscopy and centrifugation experiments.

## 2. Experimental

### 2.1. Material

Phyllite was obtained from the uranium mining site Schlema-Alberoda near Aue in Western Saxony. It was collected 540 m below ground and represents a typical, light-colored phyllite of this mining site (Wildner, 1996). The minerals of phyllite are very tightly intergrown with each other so that is not possible to separate them and extract pure minerals from the phyllite. Albite and muscovite were obtained as geological specimens. Quartz was a commercially available fine-grained quartz (Merck, p.a.) with a grain size of 0.2–0.8 mm, which was already washed and calcined. Phyllite and the minerals quartz, muscovite, and albite were ground and sieved with mesh sizes of 2 mm, 630, 200, 63, and 20  $\mu\text{m}$ . The 63–200- $\mu\text{m}$  fractions were used in the batch sorption experiments. Chlorite was collected from a granite fracture at Grimsel, Switzerland. The chlorite material was passed through a 40- $\mu\text{m}$  sieve, and was an almost pure chlorite with impurities below 10%, mostly of quartz and albite. It was identified as a ferrous iron-rich chlorite of the species ripidolite (Arnold et al., 1998). The < 40- $\mu\text{m}$  fraction was used in the batch experiments.

### 2.2. Acid–base titration

Acid–base titrations of quartz, chlorite, muscovite, and albite feldspar were performed under nitrogen atmosphere. One gram of the respective mineral phase with the grain size of 63–200  $\mu\text{m}$ , the fraction < 40  $\mu\text{m}$  for chlorite, was titrated with acid and base in 80-ml 0.1 M  $\text{NaClO}_4$  solution. Sixty microliters of 1 mM NaOH or HCl was added to the mineral suspension in intervals of 2 min, and the pH was then recorded.

### 2.3. Adsorption isotherms

The adsorption isotherms of quartz, chlorite, muscovite, and albite were determined at pH 6.5 under the following experimental conditions: half-a-gram of the respective mineral phase of the 63–200- $\mu\text{m}$  fraction (chlorite is < 40  $\mu\text{m}$ ) was added to 20 ml of 0.1 M  $\text{NaClO}_4$  solution in 50-ml polypropylene centrifuge tubes. The mineral samples were conditioned for 24 h with this solution. Then, 20 ml of 0.1 M  $\text{NaClO}_4$  solution was added to reach a final volume of 40 ml. The pH was adjusted to 6.5. The pH was checked after 24 h and, if necessary, readjusted. This was repeated until the pH was stable. Then, the uranyl–perchlorate solution was added to set the final U(VI) concentration to the desired value. The concentrations used were  $1 \times 10^{-7}$ ,  $5 \times 10^{-7}$ ,  $1 \times 10^{-6}$ ,  $5 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ , and  $5 \times 10^{-4}$  M. Immediately after the

addition of the uranium, the pH was readjusted to 6.5. Then, the samples were rotated end-over-end at 1–5 rpm for about 60 h to minimize abrasion and to keep the geomaterial in suspension. After 60 h, the final pH value was measured, and the aqueous phase and the solid phase were separated by centrifugation at 3000 rpm for 7 min. Subsequently, the supernatant was filtered using Centriscart C 30 membranes with a pore size of approximately 5 nm. The filtrate was acidified to a pH of about 1.5, and the sample was analyzed for uranium by ICP–MS. Surface site densities were evaluated at pH 6.5 and an initial uranium concentration of  $1 \times 10^{-4}$  M.

#### 2.4. Batch sorption experiments

Batch sorption experiments with uranyl and phyllite, in addition to quartz, chlorite, muscovite, albite, and ferrihydrite, were carried out under ambient temperature and pressure in the pH range of 3.5–9.5 in 0.1 M NaClO<sub>4</sub> solution. An U(VI) concentration of  $1 \times 10^{-6}$  M, a size fraction of 63–200  $\mu\text{m}$  (chlorite is  $< 40 \mu\text{m}$ ), and a solid/solution ratio of 0.5 g:40 was used. Batch sorption experiments with ferrihydrite were carried out with a 1 mM Fe suspension. The preparation of ferrihydrite was described in detail in Reich et al. (1998). To speed up equilibration with atmospheric CO<sub>2</sub>, a defined amount of NaHCO<sub>3</sub>, calculated with the equilibrium speciation computer code HYDRAQL (Papellis et al., 1988), was added to the samples, which were adjusted to pH values  $\leq 7$ . A detailed description of the experimental conditions used in the batch experiments is given in Arnold et al. (1998). The experimental error from the ICP–MS analysis was 7.5%, for a uranium concentration of  $1 \times 10^{-6}$  M, and 12.5% for  $1 \times 10^{-7}$  M uranium.

#### 2.5. Mössbauer spectroscopy

A phyllite powder of the fraction 63–200  $\mu\text{m}$  was measured with transmission Mössbauer spectroscopy (TMS) analysis before and after the sorption experiments. The TMS measurements were carried out at room temperature. It is a conventional spectrometry in the constant acceleration regime, and had nominally 3.7 GBq. The source used was <sup>57</sup>Co in a Rh matrix. A quadrupole splitting of  $> 2 \text{ mm/s}$  is characteristic of Fe(II), while a quadrupole splitting of 0.5–0.8 mm/s is indicative of Fe(III). The spectra were computer-fitted with two Fe(II) quadrupole doublets and two Fe(III) quadrupole doublets.

#### 2.6. Centrifugation experiments

Ten grams of the phyllite powder, 63–200  $\mu\text{m}$  fraction, were suspended in 250 ml of water. This mixture was shaken for 1 day. Aliquots of the phyllite suspension were centrifuged at varying centrifugal forces ( $1\text{--}46\,000 \times g$ ) in a Centrificon T 124 high-speed centrifuge (Kontron Instruments, Neufahrn, Germany). A fixed-angle rotor (angle 34°) was used. Well-defined volumes of the centrifugate were removed from the centrifugal tubes and analyzed for Fe, Al, Si, Mn, Na, K, Ca, and Mg by ICP–MS, and AAS (Na, K, Fe, Ca).

### 2.7. Specific surface area

A method described by Haul and Dümbsgen (1960), based on the BET method, was used to determine the specific surface area of phyllite, quartz, muscovite, albite (63–200  $\mu\text{m}$  fraction), and chlorite (< 40- $\mu\text{m}$  fraction), by heating the sample to 200°C and, subsequently, adsorb nitrogen to the solid surface. The experimental error of this method is 5–10%.

## 3. Results and discussion

The phyllite is composed of 48 vol.% quartz, 25 vol.% chlorite, 20 vol.% muscovite, 5 vol.% albite feldspar, and 2 vol.% opaque material, mostly rutile, magnetite, and traces of hematite (Arnold et al., 1998). Based on the mineralogical composition of the phyllite, separate batch sorption experiments were conducted with the phyllite main mineralogical constituents, i.e. the pure mineral phases, quartz, chlorite, muscovite, and albite. The opaque minerals, magnetite and rutile were not considered because these minerals are not very reactive and their mass is very small, so that their influence on the uranyl sorption onto phyllite was considered to be negligible.

To apply the diffuse double layer model (DDLDM), various parameters of each mineral were first determined. These parameters are: the specific surface area, the surface site density of the uranyl complexation sites, and the respective surface acidity constants. The specific surface area of the mineralogical main components of the phyllite are shown in Table 1 and range from 0.2  $\text{m}^2/\text{g}$  for quartz and albite, to 1.4  $\text{m}^2/\text{g}$  for muscovite, to 1.8  $\text{m}^2/\text{g}$  for chlorite. The specific surface area of phyllite was also determined as 4.0  $\text{m}^2/\text{g}$ , which is distinctively higher than any of its main mineralogical components.

The total site density of the mineral surfaces were determined from adsorption isotherms at pH 6.5 in 0.1 M  $\text{NaClO}_4$  solution using initial uranium concentrations between  $1 \times 10^{-7}$  and  $5 \times 10^{-4}$  M uranium. The total site concentration was assessed at pH 6.5 with an initial uranium concentration of  $1 \times 10^{-4}$  M, and a solid concentration of 500 mg/40 ml (Zorn, 2000). The determined site densities of quartz, chlorite, muscovite, and albite are also listed in Table 1.

Table 1  
Specific surface area and surface site density of the main mineralogical constituents of the phyllite determined from adsorption isotherms

Mineral	Specific surface area ( $\text{m}^2/\text{g}$ )	Surface site density (sites/ $\text{nm}^2$ )
Quartz	0.2	4.81
Chlorite	1.8	1.45
Muscovite	1.4	2.61
Albite	0.2	3.10 <sup>a</sup>

<sup>a</sup>This value is taken from the adsorption of  $\text{H}^+$  on albite, not from adsorption isotherms.

The surface acidity constants of quartz, chlorite, muscovite, and albite were determined by individual acid–base titrations (Arnold et al., 1999a,b; Zorn, 2000). The constants are shown in Table 2. These surface acidity constants, together with a postulated cation exchange constant for albite and the experimental data from the batch sorption experiments, were used to calculate surface complex formation constants describing the sorption of uranium(VI) onto the respective mineral surfaces. The computer code FITEQL Version 3.2. (Herbelin and Westall, 1996) was used to optimize the thermodynamic constants. Based on speciation calculations of  $1 \times 10^{-6}$  M U(VI) and an ionic strength of 0.1 M, the following six possible surface complexes were considered for the modeling: Three mononuclear monodentate surface species  $(\text{XOUO}_2)^+$ ,  $(\text{XOUO}_2\text{OH})^0$ , and  $(\text{XOUO}_2(\text{OH})_2)^-$ , and three mononuclear bidentate surface species  $(\text{XO}_2\text{UO}_2)^0$ ,  $(\text{XO}_2\text{UO}_2\text{OH})^-$ , and  $(\text{XO}_2\text{UO}_2(\text{OH})_2)^{2-}$ . However, only the monodentate mononuclear  $(\text{XOUO}_2)^+$  and the bidentate mononuclear  $(\text{XO}_2\text{UO}_2)^0$  surface complexes were important to fit the experimental data. Fig. 1 shows the results of the batch sorption experiments with the respective minerals, together with fitted sorption curves based on the calculated surface complex formation constants, using stability constants for uranium speciation in solution of Grenthe et al. (1992). The modeling slightly underpredicts the sorption maxima of all curves. Including cation exchange reactions, reactions related to the adsorption of  $\text{CO}_2$  onto the mineral surfaces, and the possible formation of ternary complexes of uranyl–carbonate–mineral surface species would improve the fit, especially for chlorite and albite. Unfortunately, such constants are so far, not available. The calculated surface complex formation constants of quartz, chlorite, muscovite, and albite are summarized in Table 3.

FITEQL calculations were carried out for a composite phyllite which was constructed from the respective mineral components, quartz, chlorite, muscovite, and albite in their relative proportion within the phyllite. Fig. 2 shows the calculated sorption curve of the composite phyllite. The composite phyllite predicts the pH region in which uranyl sorption takes place fairly well, however, it significantly underestimates the amount of uranyl(VI) sorbed onto the phyllite. This indicates that at least one of the pure mineral components does not sufficiently represent the phyllite and/or one minor component having a significant ability to sorb U(VI) was omitted. Quartz, muscovite, and albite are very likely to represent the minerals in the phyllite. However, chlorite used for our

Table 2  
Surface acidity constants of the mineralogical components of the phyllite

Mineral	Reaction	$\log K$ ( $I = 0.1$ M)	Reference
Quartz	$\text{XOH} = \text{XO}^- + \text{H}^+$	–5.62	Arnold et al., 1999a
Chlorite	$\text{XOH} + \text{H}^+ = \text{XOH}_2^+$	10.3	Zorn, 2000
Muscovite	$\text{XOH} = \text{XO}^- + \text{H}^+$	–7.81	Arnold et al., 1999a
	$\text{XOH} + \text{H}^+ = \text{XOH}_2^+$	6.06	
Albite	$\text{XOH} = \text{XO}^- + \text{H}^+$	–7.87	Arnold et al., 1999b
	$\text{NaXOH}^+ + \text{H}^+ =$	6.34	
	$\text{HXOH}^+ + \text{Na}^+$		

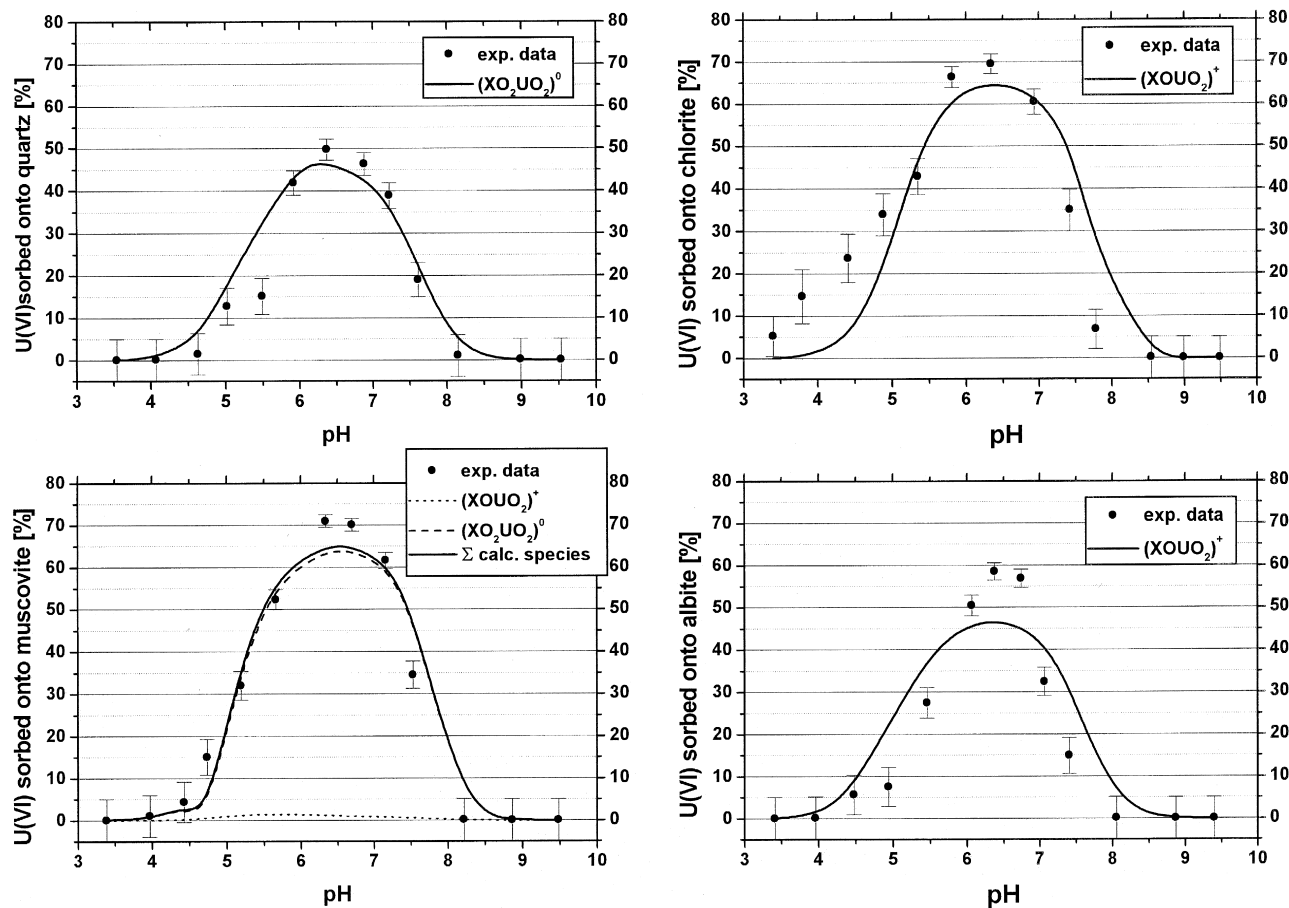


Fig. 1. Experimental results from batch sorption experiments with quartz, chlorite, muscovite, and albite together with the modeled sorption curves based on calculated surface complex formation constants of uranyl(VI) sorbing onto the respective minerals.

Table 3  
Surface complex formation constants of uranyl(VI) with the respective mineralogical component of the phyllite

Mineral	Reaction	log <i>K</i> ( <i>I</i> = 0 M)	Reference
Quartz	$X(OH)_2 + UO_2^{2+} = (XO_2UO_2) + 2H^+$	−5.51	Arnold et al., 1999a
Chlorite	$XOH + UO_2^{2+} = (XO^- UO_2^{2+})^+ + H^+$	4.71	Zorn, 2000
Muscovite	$X(OH)_2 + UO_2^{2+} = (XO_2UO_2) + 2H^+$	−0.55	Arnold et al., 1999a
	$XOH + UO_2^{2+} = (XO^- UO_2^{2+})^+ + H^+$	−5.75	
Albite	$XOH + UO_2^{2+} = (XO^- UO_2^{2+})^+ + H^+$	1.54	Arnold et al., 1999b

experimental studies does not properly represent the chlorite component in the phyllitic rock. The chlorite used for the pure mineral sorption experiments was collected as sand-like material, indicating that the material is a pedogenic chlorite. This means that water had already circulated through this material, thus extracting the most soluble elements. Therefore, the primary chlorite in the phyllite and the chlorite used as a pure mineral phase (although both being assigned to the ripidolite chlorite species) were different. Arnold et al. (1998) discusses this point in more detail. Mössbauer spectroscopy of the pedogenic chlorite, before and after the batch sorption experiments, showed that there was no change observed in the Fe(II) and Fe(III) concentration,

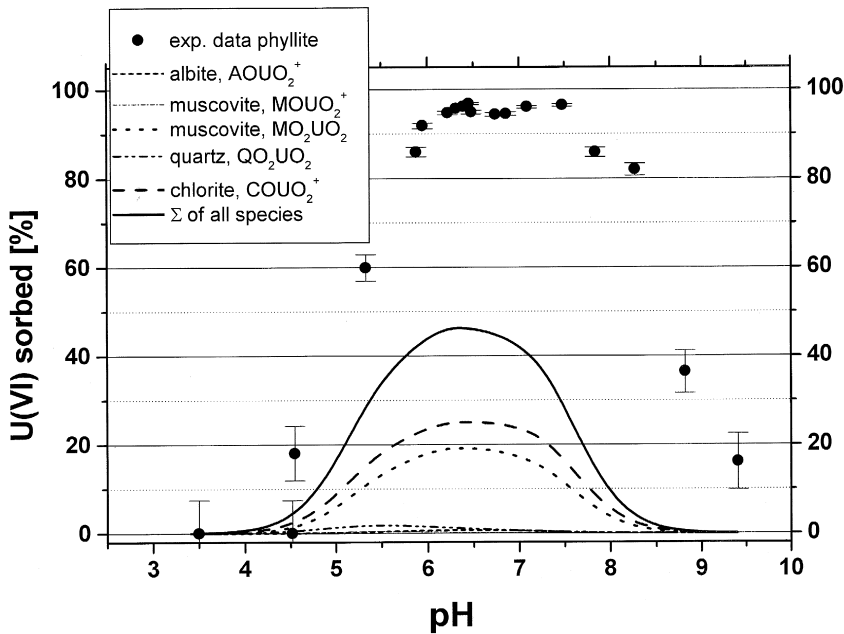


Fig. 2. Calculated uranyl(VI) sorption onto phyllite, based on surface complex formation constants of the main mineralogical phyllite components and experimental data of uranyl(VI) sorption on phyllite.



clearly indicating that this chlorite is resistant to weathering during the time span of the batch experiments. Mössbauer studies of the phyllite powder, before and after the batch experiments, however, showed a 2.8% increase in ferric iron and a simultaneous decrease in ferrous iron during the batch sorption experiment. The source of the leachable iron was exclusively the primary chlorite within the phyllite. Primary chlorites tend to weather to hydroxyl interlayered vermiculites and smectites (Barnhisel and Bertsch, 1989; Senkayi et al., 1981), thereby losing Fe(II) to the solution, which becomes oxidized to Fe(III). The Fe(III) aquo ions then polymerize to iron hydroxides through deprotonation. These precipitates consist most likely of the poorly ordered iron oxide hydroxide mineral ferrihydrite. The chemical formula of ferrihydrite is still under debate. Currently, three formulas are proposed:  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$  (Towe and Bradley, 1967),  $\text{Fe}_5(\text{O}_4\text{H}_3)_3$  (Chukhrov et al., 1973), and  $\text{Fe}_2\text{O}_3 \cdot 2\text{FeOOH} \cdot 2.6\text{H}_2\text{O}$  (Russell, 1979). Two types of ferrihydrite are currently distinguished. A two-line ferrihydrite and a six-line ferrihydrite, depending on their XRD pattern (Schwertmann et al., 1999). These ferrihydrites have particulate sizes of 4–6 nm for the six-line ferrihydrite (Russell, 1979) and 2–3 nm for the two-line ferrihydrite (Zhao et al., 1993). This explains the large specific surface area reported at  $600 \text{ m}^2/\text{g}$  (Waite et al., 1994). The weathering of a phyllite was studied by Gilkes and Little (1972). The main change during phyllite weathering is the progressive degeneration of the chlorite mineral to vermiculite by oxidation of ferrous iron and the loss of iron and magnesium from the brucite layer. The iron is transported to the edges of the phyllite fragments where it precipitates, often forming a hard reddish-brown crust or rusty laminae, indicative for Fe-oxide or Fe-hydroxide minerals. It is very likely that some iron was leached from the chlorite and may have been precipitated as ferrihydrite. This is supported by the observation of a very thin film with reddish-brownish color which formed in the course of the batch sorption experiments. Formation of Fe-minerals during chlorite weathering was also observed in nature. Ohnuki et al. (1995) found, in the vicinity of the Koongarra ore deposit, Australia, that migrating uranium becomes fixed to sorption sites of Fe-minerals produced during chlorite weathering.

Indirect evidence for the formation of ferrihydrite in the course of the batch experiments was obtained with Mössbauer spectroscopy conducted at ambient temperature on two samples. The first sample was phyllite powder before the sorption experiment, i.e. that was not in contact with water, and the second one was a phyllite sample after the batch experiments, i.e. after a percolation time of about 6 weeks. The transmission Mössbauer spectrum showed an increase in ferric iron from  $20.3 \pm 1.0\%$  in the untreated sample to  $23.1 \pm 1.9\%$  in the sample after the batch experiment. This 2.8% increase of iron(III) can be attributed to the formation of ferrihydrite. The formation of hematite and goethite is highly unlikely considering the experimental conditions of the batch experiments. Using the formula of the ripidolite chlorite  $(\text{Mg}_{2.4}\text{Fe}_{2.2}\text{Al}_{1.4})\text{-(Si}_{2.5}\text{Al}_{1.4})\text{O}_{10}(\text{OH})_8$ , and knowing that 25 vol.% of the phyllite was chlorite, this 2.8% increase corresponds to 0.74 mg Fe, forming in 500 mg phyllite powder. Considering the Fe amount in ferrihydrite of 58.14 mass% Fe, 0.74 mg iron are equivalent to 1.27 mg of ferrihydrite.

Additional evidence for the formation of ferrihydrite was obtained by centrifugation experiments with various centrifugal accelerations ( $1\text{--}46\,000 \times g$ ) on a suspension of

ground phyllite. With this technique, Fe nanoparticles with diameters from 6 to 25 nm were detected (Zänker et al., 2000). Evidence was also found that iron particles below 6 nm exist. Such nanoparticles of ferrihydrite agglomerate and tend to form larger units of ferrihydrite particles.

We include the 1.27 mg ferrihydrite in the composite phyllite FITEQL calculations. Altogether, 52 species were included in the calculation, and no optimization with experimental data was performed. The ferrihydrite surface acidity and surface reaction constants used for the modeling are shown in Table 4. A value of 600 m<sup>2</sup>/g was used for the specific surface area and a total surface site density of  $8.75 \times 10^{-4}$  M for 1 mM Fe as ferrihydrite suspension, with  $1.8 \times 10^{-6}$  M strong sites and  $8.732 \times 10^{-4}$  M weak sites, taken from Waite et al. (1994), was included. Fig. 3 shows the modeled sorption curve together with the experimental sorption data of phyllite. It is noteworthy that the calculated sorption curve of the phyllite is based exclusively on surface complex formation and surface acidity constants obtained from individual batch experiments with pure mineral phases. No experimental data of phyllite were used for the optimization procedure. Including the newly formed phase ferrihydrite leads to a significant improvement of the modeled sorption curve of uranyl sorbing onto phyllite. Using the surface complexation constants of Waite et al. (1994) gave an almost identical curve.

It seems unlikely that the postulated weathering reactions take place while conducting the batch experiments. However, freshly broken mineral surfaces are more susceptible to weathering than natural mineral surfaces, and the specific surface area of ground minerals are much larger than those of their natural counterparts. This may compensate for the short time of a batch experiment. Furthermore, adjusting the pH in a phyllite batch experiment is a very time-consuming activity, and took about 30 times of pH readjustment before the pH was stable. This added up to about 6 weeks of weathering time. The formation of ferrihydrite coming from mineral and rock leaching may be especially important in the unsaturated zone. There, the newly forming nanosized iron particles may not migrate as colloids with the flowing water, but are cemented to the surrounding minerals. Under subsequent conditions of saturation, the nanosized iron particles are not removed and form Fe-coatings, often observed on fracture surfaces or

Table 4  
Reactions occurring on the ferrihydrite surface

Surface reactions on ferrihydrite	log <i>K</i> ( <i>I</i> = 0)	Reference
$\text{FeOH} + \text{H}^+ = \text{FeOH}_2^+$	6.51	Davis, 1977
$\text{FeOH} = \text{FeO}^- + \text{H}^+$	−9.13	Davis, 1977
$\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3 + \text{H}_2\text{O}$	2.90	Waite et al., 1994 <sup>a</sup>
$\text{FeOH} + \text{H}_2\text{CO}_3 = \text{FeCO}_3^- + \text{H}_2\text{O} + \text{H}^+$	−5.09	Waite et al., 1994
$(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{2+} = (\text{Fe}_s\text{O}_2)\text{UO}_2 + 2\text{H}^+$	−3.18	Arnold et al., 1996
$(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{2+} = (\text{Fe}_w\text{O}_2)\text{UO}_2 + 2\text{H}^+$	−6.31	Arnold et al., 1996
$(\text{Fe}_s(\text{OH})_2) + \text{UO}_2^{2+} + \text{CO}_3^{2-} = (\text{Fe}_s\text{O}_2)\text{UO}_2\text{CO}_3 + 2\text{H}^+$	3.67	Waite et al., 1994
$(\text{Fe}_w(\text{OH})_2) + \text{UO}_2^{2+} + \text{CO}_3^{2-} = (\text{Fe}_w\text{O}_2)\text{UO}_2\text{CO}_3 + 2\text{H}^+$	−0.42	Waite et al., 1994

<sup>a</sup>Calculated from experimental data of Zachara et al. (1987).

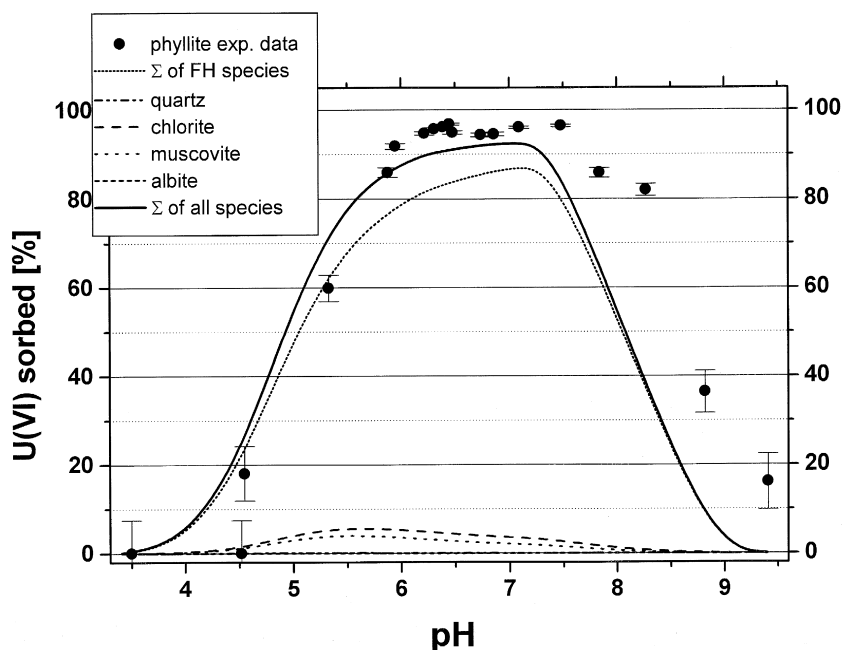


Fig. 3. Modeled uranyl(VI) sorption onto phyllite together with experimental uranyl(VI) sorption data on phyllite. The modeled curve is calculated using surface complex formation constants of uranyl(VI) sorbing onto quartz, chlorite, muscovite, albite, and ferrihydrite.

mineral grains in nature (Payne et al., 1994). These coatings, however, may be in nature, a mixture of originally forming ferrihydrite, which transforms with time to the thermodynamically more stable iron minerals, hematite and goethite. These transformation reactions are significantly retarded by the adsorption of silicate and organic macromolecules onto ferrihydrite.

#### 4. Conclusions

The sorption of uranyl(VI) onto rocks can be modeled by using SCM. This model uses the interactions of the individual pure mineral components with the uranyl(VI) ion which are determined from individual batch sorption experiments. The so derived constants were used to create the composite phyllite. However, mineral dissolution reactions and formation of new secondary phases also have to be included. Secondary phases may form very small amounts of a new solid, but the small size of these newly formed particles may result in a large specific surface area, and thus may be very important for the sorption process. Their identification and quantification is very important to successfully model the sorption of uranyl(VI) onto the phyllite, and probably other rock systems.

Our approach appears quite promising for the description of other rock systems because the number of rock forming minerals in nature is rather small (Matthes, 1983). Assembling a database containing all relevant information of common rock-forming minerals would be a highly desirable prerequisite. Such a database should contain surface complexation constants of respective minerals and metal contaminants. Relevant cation exchange reactions, surface acidity constants, and constants describing the CO<sub>2</sub> adsorption on mineral surfaces must also be included. Furthermore, the formation of ternary complexes, especially respective mineral–carbonate–metal surface complexes, and detailed information of possible secondary phase formation should be part of such a database.

We have shown that the sorption of uranium(VI) onto phyllitic rock can be very well described by delineating the sorption process into sorption processes of the rock's components. This approach should also be applicable to describing the sorption of radionuclides and metals to other rock materials.

### Acknowledgements

The authors would like to thank G. Grambole for acid–base titration, G. Hüttig for centrifugation experiments, W. Wiesener and A. Schäfer for ICP–MS and AAS analysis, G. Schuster for BET measurements, and H. Reuther for Mössbauer measurements. Phyllite samples and chlorite samples (< 40-μm fraction) were kindly provided by G. Wildner (Wismut) and Prof. Van Gunten, respectively. These studies were funded by the Deutsche Forschungs Gemeinschaft (DFG) under the project number Ni 210/6-1.

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